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Effect of Oxalate on the Dissolution Rates of Oligoclase and Tremolite (Journal Version)

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16. ABSTRACT

The effect of oxalate, a strong chelator for Al and other cations, on the dissolution rates of oligoclase feldspar and tremolite amphibole was investigated in a flow-through reactor at 22°C. Oxalate at concentrations of 0.5 and 1 mM has essentially no effect on the dissolution rate of tremolite, nor on the steady-state rate of release of Si from oligoclase. The fact that oxalate has no effect on dissolution rate suggests that detachment of Si rather than Al or Mg is the rate-limiting step. At pH 4 and 9, oxalate has no effect on the steady-state rate of release of Al, and dissolution is congruent. At pH 5 and 7, oligoclase dissolution is congruent in the presence of oxalate, but in the absence of oxalate Al is preferentially retained in the solid relative to Si.

Large transient "spikes" of Al or Si are observed when oxalate is added to or removed from the system. The cause of the spikes is unknown; we suggest adsorption on feldspar surfaces away from sites of active dissolution as a possibility. Solutions in the reactors are undersaturated with respect to both gibbsite and kaolinite, so neither the spikes nor the incongruent dissolution can be explained by formation of a secondary precipitate.

The rate of dissolution of tremolite is independent of pH over the pH range 2-5, and decreases at higher pH. The rate of dissolution of oligoclase in our experiments was independent of pH over the pH range 4-9. Since the dissolution rate of these minerals is independent of pH and organic ligand concentration, the effect of acid deposition from the atmosphere on the rate of supply of cations from weathering of granitic rocks should be minor.

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JOURNAL ARTICLE

The effect of oxalate on the dissolution rates of oligoclase and tremolite

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Abstract—The effect of oxalate, a strong chelator for Al and other cations, on the dissolution rates of oligoclase feldspar and tremolite amphibole was investigated in a flow-through reactor at 22°C. Oxalate at concentrations of 0.5 and 1 mM has essentially no effect on the dissolution rate of tremolite, nor on the steady-state rate of release of Si from oligoclase. The fact that oxalate has no effect on dissolution rate suggests that detachment of Si rather than Al or Mg is the rate-limiting step. At pH 4 and 9, oxalate has no effect on the steady-state rate of release of Al, and dissolution is congruent. At pH 5 and 7, oligoclase dissolution is congruent in the presence of oxalate, but in the absence of oxalate Al is preferentially retained in the solid relative to Si.

Large transient "spikes" of Al or Si are observed when oxalate is added to or removed from the system. The cause of the spikes is unknown; we suggest adsorption on feldspar surfaces away from sites of active dissolution as a possibility. Solutions in the reactors are undersaturated with respect to both gibbsite and kaolinite, so neither the spikes nor the incongruent dissolution can be explained by formation of a secondary precipitate.

The rate of dissolution of tremolite is independent of pH over the pH range 2–5, and decreases at higher pH. The rate of dissolution of oligoclase in our experiments was independent of pH over the pH range 4–9. Since the dissolution rate of these minerals is independent of pH and organic ligand concentration, the effect of acid deposition from the atmosphere on the rate of supply of cations from weathering of granitic rocks should be minor.

INTRODUCTION

PREDICTION OF THE effects of deposition of acidic compounds from the atmosphere on the chemistry of surface waters is currently a topic of great concern (*e.g.* SCHNOOR, 1984; REUSS and JOHNSON, 1986). Chemical weathering of minerals is the major process that neutralizes acid deposition over long periods of time. In order to predict the future impact of acid deposition on surface waters it is important to understand: 1) the present-day rates of chemical weathering in "sensitive" areas, and 2) the effect of an increase in the input of acidity on these rates. The effect of organic compounds on dissolution kinetics is presently a key unknown in our ability to predict the effect of an increase in acidity on weathering rates. It has long been recognized that organic chelators play an important role in the transport and distribution of aluminum and iron in soil horizons. In solutions collected from some North American soils, high concentrations of aluminum and base cations (Ca, Mg, Na, and K) show a strong positive correlation with high concentrations of dissolved organic compounds (GRAUSTEIN, 1981; ANTWEILER and DREVER, 1983; CRONAN, 1984). Based on these observations the authors hypothesized organic acids/anions might actually be controlling the weathering rate of primary minerals in the upper soil zone through both complexation and the effect of organic acids on solution pH.

Several specific mechanisms have been hypothesized for the effect of organic acids on the rate of dissolution of aluminosilicates. If the rate-controlling process is detachment of an aluminum-containing species from the surface of the solid (BERNER and HOLDREN, 1979; BERNER *et al.*, 1985; AAGAARD and HELGESON, 1982; HELGESON *et al.*, 1984; STUMM *et al.*, 1985), complexation of Al on the surface of the solid should accelerate dissolution, as is observed for aluminum oxide (FURRER and STUMM, 1986). Conversely, if dissolution rate is controlled by diffusion through an aluminum-containing secondary layer (*e.g.* WOLLAST, 1967; CHOU and WOLLAST, 1984), chelating ligands might increase the solubility of aluminum and inhibit the formation of the secondary layer.

Several laboratory studies have investigated the effects of organic ligands on the weathering rates of silicate minerals (HUANG and KELLER, 1970; HUANG and KIANG, 1972; GRANDSTAFF, 1986; MANELY and EVANS, 1986). The general conclusion has been that organic acids catalyze the dissolution reaction. Interpretation of previous studies is often complicated by aspects of the experimental design. For example, some authors failed to buffer pH, making it difficult to separate out the effects of pH from those of complexation (HUANG and KELLER, 1970; HUANG and KIANG, 1972; MANELY and EVANS, 1986). Others used high concentrations of organic compounds not commonly found in nature (HUANG and KELLER, 1970; HUANG and KIANG, 1972; GRANDSTAFF, 1986) and most studies were conducted in batch-type reactors, which allow solute concentrations to change as a function of time. Solutions usually became saturated with respect to secondary precipitates, which greatly complicates interpretation of changes in solute concentration with time (*e.g.* HOLDREN and ADAMS, 1982).

The goal of this study was to investigate the effect of an organic chelator and pH on the dissolution rates of oligoclase feldspar and tremolite (an amphibole that is structurally analogous to hornblende but contains only Mg as a major cation) using a flow-through reactor

of the type first introduced by CHOU and WOLLAST (1984). Feldspars and amphiboles are both important sources of cations to surface waters, particularly in areas where weathering rates are low (APRIL *et al.*, 1986; DREVER and HURCOMB, 1986; CLAYTON, 1986). Experiments were performed under various pH conditions in dilute solutions containing oxalate. Oxalate is a strong chelator of aluminum and other cations, and is commonly found in soil solutions (GRAUSTEIN *et al.*, 1977). Silicate minerals placed in laboratory cultures of oxalate-producing fungi have undergone rapid alteration (ECKHARDT, 1979; JONES *et al.*, 1980; WILSON *et al.*, 1981), although the relative importance of chelation and pH (which dropped to below 2 in some experiments) has not been established. Although feldspar dissolution rates have been extensively studied in the past, the pH-dependence of the dissolution rate in the environmentally critical region around pH 4 is not well defined (see, for example, CHOU and WOLLAST, 1985; KNAUSS and WOLERY, 1986).

MATERIALS AND METHODS

Fluidized bed reactor

Experiments in this study were conducted in a fluidized bed flow-through type reactor (Fig. 1) similar to that of CHOU and WOLLAST (1984). The slow pump (Fig. 1) operating at around 0.1 ml/min adds fresh solution to the reactor and removes reacted solution at the same rate. The fast pump serves to keep the mineral grains suspended and the solution well mixed. 4 g of solid phase were used in each run; the volume of solution in the reactor was 25 ml. There are several advantages with this design over a conventional batch reactor. Due to the constant turnover of solution in the reactor, concentrations of dissolved components eventually reach a steady state and can be maintained below saturation with respect to possible precipitates. In addition, the composition of the input solution can be changed in order to test the effect of different solution compositions on the same batch of solid phase.

Solid material

We conducted our experiments with an oligoclase feldspar from Bancroft, Ontario and a tremolite from New York both obtained from Wards Natural Establishment. Thin sections were prepared for each sample and chemical composition was determined by electron microprobe analysis (Table 1). Optical microscopy revealed that the oligoclase contained small amounts of muscovite and had been subjected to minor sericitization. Albite twins exhibited a moderate amount of kinking and fracturing. The composition of the oligoclase is An_{13}. Sodic plagioclase in the compositional range An_5–An_{18} falls within the peristerite exsolution field and should exsolve into two phases of about An_{0-1} and An_{25-28} (HYNDMAN, 1972). We were not able to observe the exsolved phases in thin section; peristerite rarely shows exsolution on a visible scale. The tremolite was found to contain a significant amount of fine-grained quartz. The sample was estimated to contain 33% quartz by comparing the microprobe analyses to a bulk chemical analysis of the size-fractionated material. As it was not possible to separate the two minerals, we conducted an experiment to check the possibility that quartz dissolution would be a significant source of silicon. In alkaline solutions it dissolved rapidly enough to affect the results of the tremolite experiments but under acidic conditions the release rate of silicon from quartz was negligible.

Table 1. Chemical analyses and surface area measurements of mineral samples.

mineral	oligoclase		tremolite	
chemical composition (% weight)	SiO_2	65.06	SiO_2	60.60
	Al_2O_3	22.07	Al_2O_3	0.13
	FeO	0.02	FeO	0.17
	Na_2O	10.32	Na_2O	0.16
	CaO	2.63	CaO	0.55
	K_2O	0.14	MnO	3.78
			MgO	32.38
surface area	.116 m^2/g		.057 m^2/g	
size fraction	100-200 mesh		100-200 mesh	
sample weight	4 g		2.7 g*	

* 4 gram total sample corrected for 33% quartz content

Samples for the experiments were prepared by breaking large pieces of each mineral into smaller chunks with in an iron mortar and pestle. These large fragments were dry ground in an alumina mortar to a smaller size fraction (16–40 mesh) and then hand-picked under a binocular microscope to remove impurities. This cleaned fraction was reground in the alumina mortar and the 100–200 mesh size fraction was separated by wet sieving through nylon sieves and ultrasonically cleaned to remove ultra-fine particles. Specific surface area was determined by a 3 point B.E.T. gas adsorption method (Table 1). For surface areas below 0.2 m^2/g the uncertainty of this technique may be as great as 20%.

Solutions

Solutions in the acidic range (pH 2–5) were prepared with dilute HCl. Solutions of 0.15 mM $KHCO_3$ and 5 mM H_3BO_3 + 5 mM KOH were used to buffer at pH 7 and 9, respectively. Oxalate solutions were prepared from reagent-grade ammonium oxalate. Oxalate itself acted as a good buffer at pH 4; at pH 5 sodium acetate was added at a concentration of 0.5 mmolar to buffer the pH. 1 ppm Hg as phenylmercuric acetate was added to the organic solutions to retard microbial growth. Oxalate concentrations in the output were monitored by liquid chromatography (Dionex). We did not adjust for ionic strength in the dilute acidic solutions and variable pH experiments, as several studies have shown that far from equilibrium dissolution rate does not depend on ionic strength (LASAGA, 1984; SCHOTT *et al.*, 1981).

Analytical methods

All experiments were run under conditions of room temperature (22 ± 2°C) and pressure. Samples were collected through a 0.45 um filter on roughly a daily basis in acid-

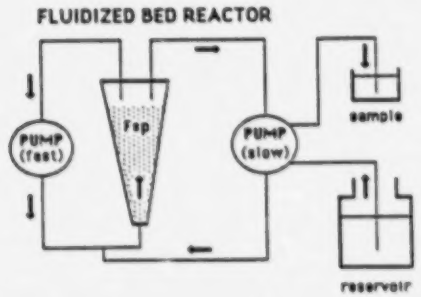

FIG. 1. Fluidized bed flow-through reactor (modified after CHOU and WOLLAST, 1984). Fsp represents feldspar (or tremolite).

washed polyethylene bottles. After a small aliquot was removed to measure pH, the sample was acidified with Ultrex™ nitric acid to a pH of 3 and stored at 4°C. Silicon was measured colorimetrically with a modified molybdate blue method. Aluminum was determined by graphite furnace atomic absorption. Ca, Na, and Mg were determined by flame AA after adding an excess of $SrCl_2$ to minimize ionization (La forms a precipitate with oxalate). Detection limits are 2 ppb for Si, 1 ppb for Al, 2 ppb for Na, 3 ppb for Ca and 1 ppb for Mg.

RESULTS AND DISCUSSION

The results of two sets of experiments are presented in this paper. In the first set, solution pH was held constant while oxalate concentration was changed to investigate the effect of organic ligands on the dissolution rate of oligoclase and tremolite. In the second set, we conducted experiments with tremolite under variable pH conditions to investigate the pH dependence of dissolution rate and reaction stoichiometry.

In all experiments the concentrations of Al, Ca, and Mg were very much less than the concentration of oxalate, so the effect of these cations on oxalate speciation is negligible.

Effect of oxalate

a) Steady-state dissolution rate. The effect of oxalate on the dissolution rate of oligoclase at pH 4, 5, 7 and 9 is shown in Fig. 2. The results are presented as the release rate of silicon and aluminum expressed in picomoles/m^2/sec *versus* time in hours. Arrows indicate the period during which oxalate was present or absent from solution. Initially each reaction was allowed to establish a steady state under constant pH conditions. The addition of oxalate has little effect on the release rate of silicon at any pH investigated. Aluminum, however, responds in a very different manner. A large transient aluminum "spike" is observed when oxalate is first added to the reactor. In the pH 4 run, the aluminum concentration gradually returns to the same steady-state value. At pH 5 and 7 the steady-state release rate is slightly elevated in the presence of oxalate and remains so for the duration of the experiment. At pH 9 there is no spike of aluminum and the steady-state rate is unaffected by the presence of oxalate.

We conducted similar experiments with the mineral tremolite. Figures 3 and 4 show the effects of oxalate on the dissolution rate of tremolite at pH 4 and 7. At concentrations of 1 mmolar oxalate has essentially no effect on the release rate of either magnesium or silicon. The apparent slight decrease in the release rate of magnesium at pH 7 may be due to the fact that the pH was difficult to buffer at 7 and rose slightly from 7.15 to 7.3 over the course of the run. Notice also that, unlike with oligoclase, there are no spikes of either magnesium or silicon when oxalate is added or removed from the system.

There are conflicting results in the literature concerning the effects of organic ligands on the dissolution rate of silicate minerals. Our studies, conducted in a flow-through reactor, show that 1 mmolar oxalate has only a slight effect on the dissolution rate of oligoclase at pH 4–9 and tremolite at pH 4 and 7. In the only other study using a flow-through type system the pH was not buffered and ranged from 3.8–4.4 depending on the organic acid used. However, the strength of the acid appeared to be more important in the release of elements from feldspar minerals than the ability of the acid to complex aluminum (MANELY and EVANS, 1986). Only a few studies of the effect of organic anions have been conducted in batch reactors under constant pH conditions. GRANDSTAFF (1986) reported that 10^{-5} to 10^{-1} M solutions of EDTA, oxalate and fulvic acid

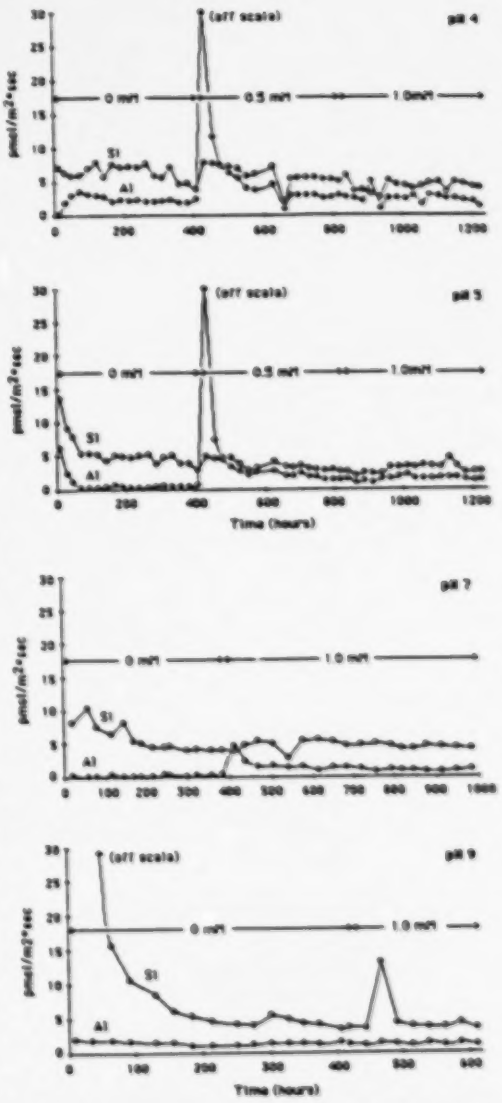

FIG. 2. Release rate of Si and Al from oligoclase in picomoles/m^2/sec as a function of time at pH 4, 5, 7 and 9 in concentrations of 0, 0.5 and 1.0 mM oxalate.

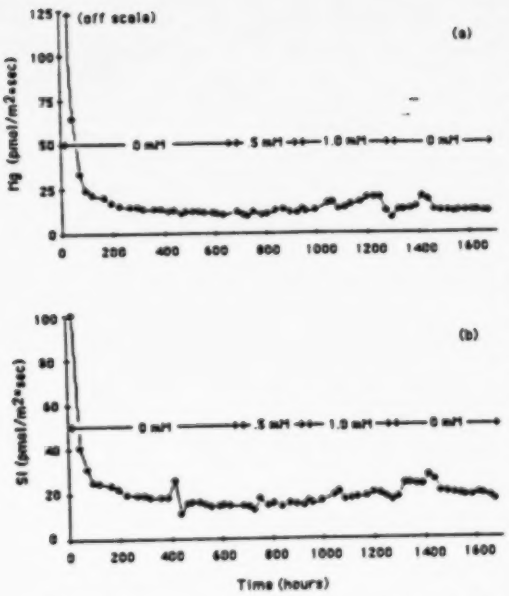

FIG. 3. Release rate of (a) Mg and (b) Si from tremolite in picomoles/m^2/sec as a function of time at pH 4 in concentrations of 0, 0.5 and 1.0 mM oxalate.

caused a significant increase in the dissolution rate of olivine under mildly acidic conditions. For example, at pH 4.5 1 mM oxalate was capable of increasing the dissolution rate by a factor of 30 relative to KCl solutions at the same pH. Not all batch studies report an increased rate with organic acids. In a previous investigation, GRANDSTAFF (1977) found that 0.1 M citrate had little effect on the rate of bronzite dissolution at pH 3 compared to HCl-KCl solutions. In addition, SCHOTT *et al.* (1981) reported that 0.2 M potassium hydrogen phthalate did not influence mineral dissolution rates of some magnesium silicate minerals over the pH range 3–6. The minerals used in Schott's study were all relatively iron free, as was the tremolite used in our experiments. The olivine used by Grandstaff, however, contained 13% FeO. It is possible that the effect with olivine was at least partly due to increased undersaturation due to strong complexing between organic ligands and Fe^{+2} (KNAUSS and WOLERY, 1986).

Oxalate has been found to enhance the dissolution rate of aluminum oxides, presumably because the formation of surface complexes weakens Al-O bonds enhancing the detachment of Al and accelerating dissolution (STUMM *et al.*, 1985; FURRER and STUMM, 1986). If the detachment of aluminum from aluminosilicates is the rate-limiting step in dissolution, then the formation of surface complexes with organic ligands should enhance dissolution. Our results suggest that this mechanism is not applicable to oligoclase feldspar dissolution and may indicate that detachment of silicon rather than aluminum is involved in the rate-limiting step. GRANDSTAFF (1986) proposed that the formation of surface complexes between magnesium and organic ligands increases the rate of olivine dissolution. Our results with tremolite provide no evidence for dissolution by this mechanism and again suggest that detachment of silicon rather than magnesium is involved in the rate-limiting step.

It is interesting to consider our results in light of the recent theory of CHOU and WOLLAST (1984, 1985), in which they proposed the formation of a residual layer at the feldspar surface during dissolution, the composition of which is strongly pH dependent. Under acidic conditions, the layer should be enriched in silica relative to aluminum and base cations. As a consequence, it has been suggested that the hydrolysis of silicon may be thought of as the rate-limiting step during dissolution (HOLDREN and SPEYER, 1985a), and the formation of ligand surface complexes might not be expected to affect the dissolution rate significantly. Under alkaline conditions, however, the composition of the depleted layer should be enriched in alumina. By similar reasoning, detachment of aluminum should be involved in the rate-limiting step, and the formation of surface complexes might be expected to enhance dissolution in much the same way as it affects the dissolution of aluminum oxides. Our results are consistent with this model in the acidic range but provide no support for the development of an aluminum-rich layer under alkaline conditions. The individual reaction steps involved in the dissolution of silicate minerals are still poorly understood, and we feel that interpretation of our results in terms of specific reaction mechanisms is largely speculative at this time.

b) Aluminum "spikes". The results of another experiment with oligoclase at pH 4 are shown in Fig. 5.

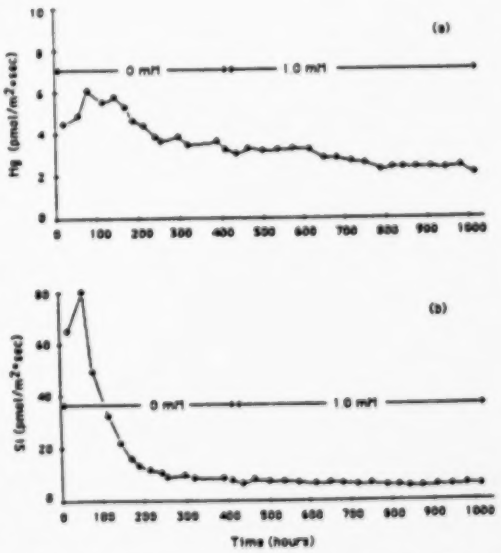

FIG. 4. Release rate of Mg (a) and Si (b) from tremolite in picomoles/m^2/sec as a function of time at pH 7 in concentrations of 0 and 1 mM oxalate.

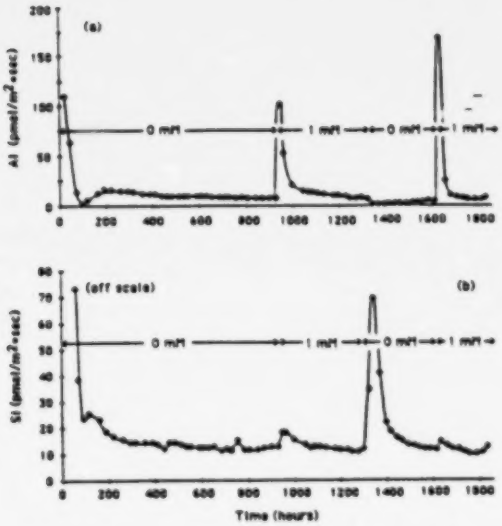

FIG. 5. Release rate of (a) Al and (b) Si from oligoclase in picomoles/m^2/sec as a function of time at pH 4 in concentrations of 0 and 1 mM oxalate.

We ran this experiment for an extended period of time under constant solution conditions to observe changes in reaction stoichiometries. Following nearly 40 days of reaction, the input composition was altered by repeatedly adding and removing oxalate in an attempt to investigate further the nature of the transient aluminum spikes. At the start of the run there is a large release of both silicon and aluminum that decreases rapidly until a steady state is approached. The high initial rate is presumably due to the dissolution of ultrafine particles not removed during cleaning, and dissolution at high-energy crystal defects. Note that aluminum goes through a minimum before reaching its steady state. We interpret its disappearance to the precipitation of a secondary phase because of pH fluctuations during the first few days. Solubility calculations (Fig. 6) show that solution compositions are initially very close to saturation with respect to both gibbsite and halloysite. As the reaction proceeds, the pH decreases and at steady state the solution composition falls well below saturation levels. At approximately 900 hours, oxalate is added to the system causing a large release of aluminum but having only a minor effect on the rate of silicon release. After the system returns to steady state, oxalate is removed from the input solution. This causes aluminum values to drop to nearly zero followed by a slow return to steady state. In contrast we observed a large "spike" of silicon followed by a quick return to steady state. The second addition of oxalate causes basically the same response as the first.

There is presently some question as to the interpretation of these spikes specifically whether they are an experimental artifact. In similar experiments using albite, CHOU and WOLLAST (1984) observed transient spikes of silicon and aluminum when they changed the pH of the input solution. They pointed out that, because it was possible to induce an elevated rate by modifying the input solution, the release could not be explained by preferential dissolution of ultra-fine particles, and attributed the spikes to an adjustment in composition of a residual layer to a change in solution composition. In our experiments, the aluminum released after oxalate is first added to the system could be explained by dissolution of material precipitated during intial stages of the reaction. This explanation, however, cannot account for the release observed when oxalate is added a second time, unless it is postulated

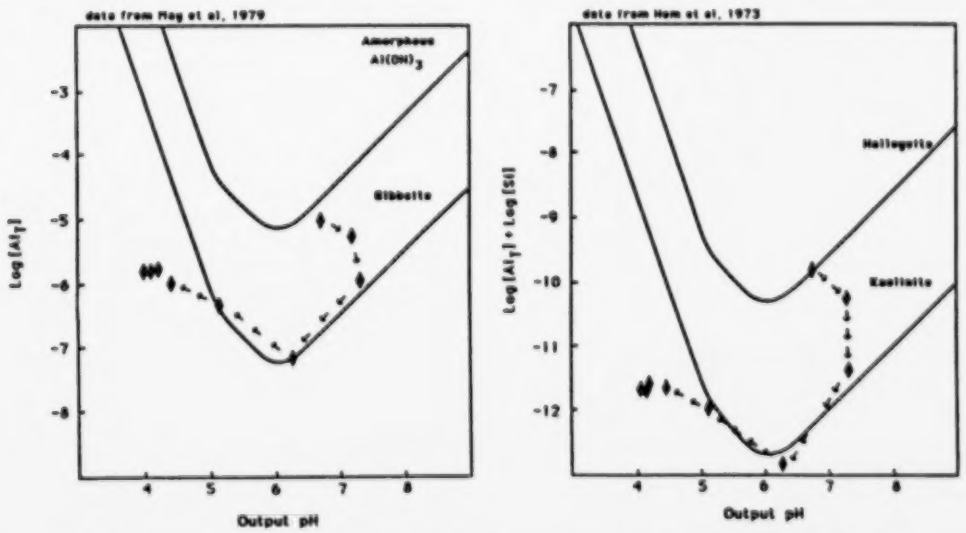

FIG. 6. Compositions of output solutions of pH 4 oligoclase experiment compared to the solubilities of $Al(OH)_3$ and $Al_2Si_2O_5(OH)_4$.

that supersaturation and precipitation occurs in a microenvironment such as an etch pit. Supersaturation in such a microenvironment would not explain the silicon spike as oxalate is removed. Some amorphous material is probably redissolved during the first spike, as nearly twice as much aluminum is released during the first spike as during the second. Another possible explanation for the spikes could be adsorption on the walls of the reactor. To test this hypothesis we conducted an experiment in which we pumped solutions containing approximately steady-state concentrations of sodium, calcium, silicon and aluminum through an empty reactor and repeated a similar experiment. Although there is a small release of aluminum and calcium when oxalate is added to the reactor it is not nearly enough to account for the large amount released in the actual experiment. The spikes appear to be related to some reaction occurring at the surface of the feldspar. They could be related either to the formation and subsequent destruction of a leached zone around dissolution sites, or to adsorption-desorption reactions on feldspar surfaces away from sites of dissolution. There is considerable literature on the adsorption and desorption of silicon at mineral surfaces (*e.g.* SIEVER and WOODFORD, 1973), although the underlying mechanisms are not understood.

Effect of pH

a) Tremolite. The results of an experiment in which the pH was varied over the range 2–5 are shown in Fig. 7. As in the oxalate experiments, there is a large release of both magnesium and silicon at the start of the run followed by a rapid approach to steady state.

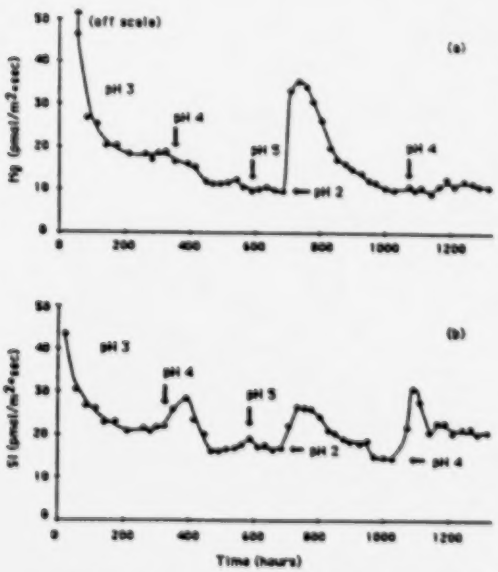

FIG. 7. Release rate of (a) Mg and (b) Si from tremolite in picomoles/m²/sec as a function of time under variable pH conditions.

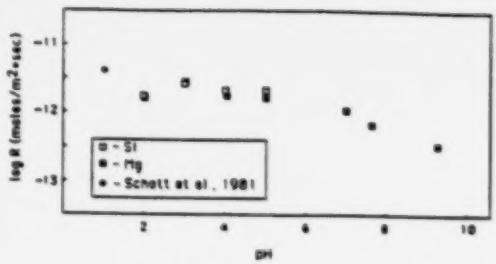

FIG. 8. Dissolution rate of tremolite in moles/m²/sec as a function of pH at 22°C.

A change in solution pH induces a transient release of solutes followed by establishment of a new steady state. It is interesting that when the pH is increased there is a transient release of silicon but not magnesium; when the pH is decreased both components are released at elevated rates.

The effect of pH on the dissolution rate of tremolite is shown in Fig. 8. The rate is essentially independent of pH over the pH range 2–5, then decreases with increasing pH between 7 and 9. The slightly higher rate observed at pH 3 might be due to the fact that it represents the first pH in the experiment, and there may be a slow decrease in the absolute rate over the several hundred hours of reaction (HOLDREN and SPEYER, 1985a). The rate at pH 1 is taken from SCHOTT *et al.* (1981) for a slightly more calcium-rich tremolite in a batch experiment. This rate is reassuringly similar to ours, as are absolute rates for some other magnesium silicate minerals (Table 2). In contrast, there is a striking difference among magnesium silicates with respect to the reaction rate dependence on a_{H^+}. Olivine and pyroxene show a strong reaction rate dependence on a_{H^+}, whereas tremolite displays an apparent zero-order dependence under acidic conditions. It is not known whether the pH independence under acidic conditions is a characteristic of the entire amphibole group.

b) Feldspar. Although most of the feldspar weathering rates from the literature are based on batch experiments, there is a growing data set available for flow-through type experiments on alkali feldspars (Fig. 9). The absolute rates from the literature are surprisingly similar to ours, even though the feldspar compositions

Table 2. Dissolution rate and dependence on a_{H^+} for some Mg-silicate minerals.

mineral	n[1]	log (rate)[2]	reference
tremolite	0 (pH 2-5)	-11.7	this study
tremolite	0 (pH 1-6)	-11.4 (pH 1)	Schott et al., 1981
enstatite	.8 (pH 1-6)	-11.4	
diopside	.7 (pH 2-6)	-9.3	
olivine	1 (pH 3-5)	-10.9	Grandstaff, 1986
bronzite	.5 (pH 1-6)		Grandstaff, 1977

[1] $r_{H^+} = k[H^+]^n$
[2] moles/m²/sec at pH 4

were different, and it may not be valid to compare surface-area-normalized rates between different size-fractions of different feldspar minerals (HOLDREN and SPEYER, 1985b). Oligoclase dissolution is apparently independent of pH over the range 4–9. HOLDREN and SPEYER (1985a) observed the reaction rate of an alkali feldspar was independent of pH between 6 and 9 then increased with decreasing pH. CHOU and WOLLAST (1985) reported albite dissolution rates that followed a pattern similar to the solubility curve for aluminum oxides. The rate was weakly dependent on pH between 5 and 8 then increased at both higher and lower values. Although there is some scatter at low pH (Fig. 9), the data are generally consistent with the model of HELGESON *et al.* (1984) and KNAUSS and WOLERY (1986), that in the intermediate pH range (2.8–8) feldspar dissolution rate has a zero order dependence on a_{H^+}; for both higher and lower pH values the rate would be pH-dependent, as indicated by the dashed lines in Fig. 9.

Reaction stoichiometries

a) Aluminum release rates. To illustrate more clearly changes in reaction stoichiometries for these runs, we have presented the data as the relative release ratio (RRR) of aluminum and cations to silicon as a function of time. The relative release ratio (RRR) is defined as

$$\log (\mathrm{RRR})_X = \log (X/\mathrm{Si})_{aq}/(X/\mathrm{Si})_{solid}$$

where (X/Si) is equal to the molar ratio of component X to Si (HOLDREN and SPEYER, 1985a). A value of zero for log (RRR) indicates congruent dissolution. Positive values correspond to a preferential release of component X to solution relative to silicon and negative values indicate a preferential release of silicon relative to component X. In our experiments with oligoclase (Fig. 10), dissolution is congruent with respect to aluminum and silicon for the entire pH 4 and 9 runs. At pH 5 and 7, however, aluminum is released at a slower rate than silicon until oxalate is added, after which point the reactions proceed congruently. Periods of incongruent dissolution have been attributed to the development of an altered layer at the mineral surface,

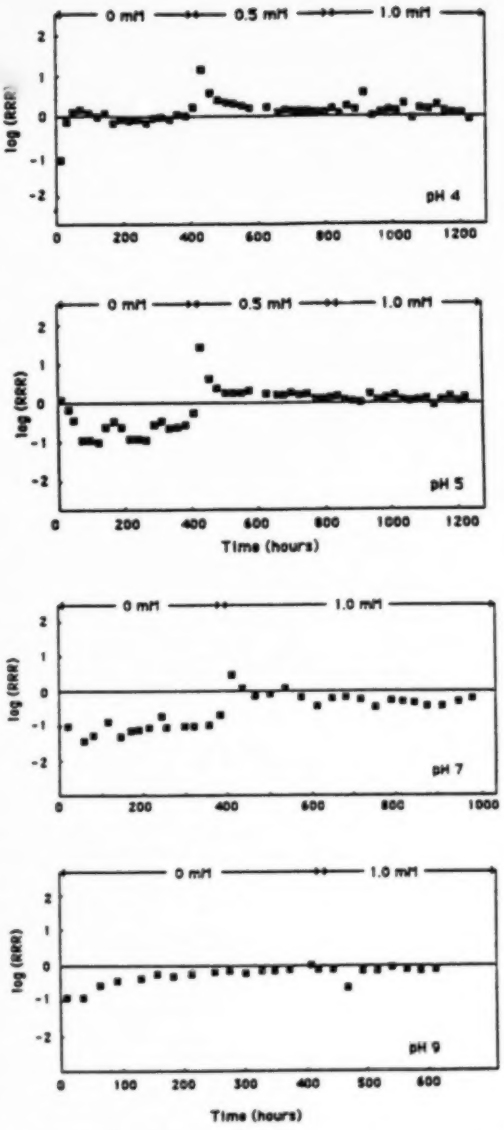

FIG. 10. Relative Reaction Rate (RRR) of Al relative to Si as a function of time for oligoclase at pH 4, 5, 7 and 9.

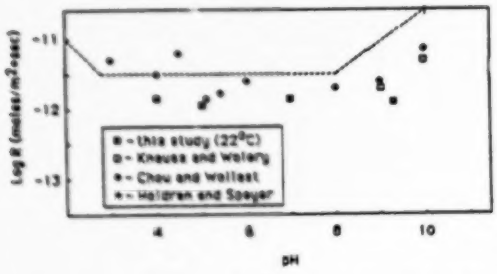

FIG. 9. Dissolution rates of some feldspar minerals in moles/m²/sec as a function of pH at 22 and 25°C. Dotted line is from HELGESON *et al.* (1984).

or, alternatively, to the formation of a discrete secondary precipitate (for a review see CHOU and WOLLAST, 1984). Solubility calculations using the computer program WATEQF indicate that solution compositions at steady state are below saturation with respect to both gibbsite and kaolinite, so it seems unreasonable to explain the period of nonstoichiometric dissolution by the formation of a secondary aluminum-containing precipitate. As mentioned previously, adsorption onto feldspar surfaces away from sites of dissolution is another potential sink for aluminum. Dissolution occurs nonuniformly over the mineral surface with prefer-

ential attack at sites of excess energy such as dislocation outcrops (HOLDREN and BERNER, 1979; BERNER *et al.*, 1985). If these active sites account for only a small fraction of the mineral surface then inactive mineral surfaces may serve as sites for adsorption. The amounts of aluminum apparently lost at pH 5 and 7, based on the difference between the aluminum concentration observed and that expected for congruent dissolution, correspond to less than 5% of a monolayer of gibbsite over the feldspar surface. We have no information on the density of potential adsorption sites at the feldspar surface, but the order of magnitude is not unreasonable.

b) Cation release rates. The rate of release of magnesium relative to silicon in the variable pH (pH 3–5) tremolite experiment is shown in Fig. 11. Initially, magnesium is released in excess of silicon presumably due to an exchange reaction between H^+ and Mg^{+2} at the fresh mineral surfaces. After steady state is reached, the reaction proceeds congruently at all pH values in this range, apart from transients following a change in solution pH. Interpretation of reaction stoichiometries under alkaline conditions was complicated by the release of silicon from quartz.

Similar behavior for the dissolution of tremolite and pyroxene in batch experiments was observed over the pH range 1–6 (SCHOTT *et al.*, 1981). An initial period of excess calcium and magnesium release was followed by an extended period of basically congruent dissolution. The authors estimated the thickness of a continuous leached layer, if it existed, would be only a few atoms thick. We calculated magnesium would be depleted to a depth of 7 Å during the initial period of incongruency at pH 3. A layer of this dimension would not be thick enough for diffusion through it to be rate-limiting, which supports the hypothesis that dissolution of tremolite is controlled by a surface reaction (SCHOTT *et al.*, 1981; SCHOTT and BERNER, 1984).

The relative rates of release of calcium, sodium and aluminum are shown in Fig. 12 for an experiment with oligoclase at pH 4. Initially, both sodium and calcium are released in excess with respect to silicon but sodium and aluminum rapidly establish steady-state values which are approximately congruent with respect to the bulk composition of the solid. Calcium on the other hand is released at a rate several times its stoichiometric

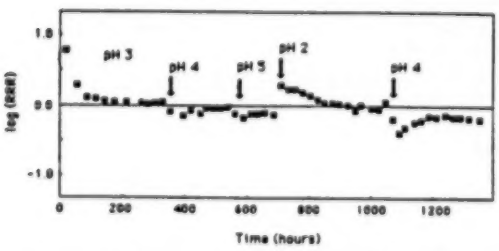

FIG. 11. Relative Reaction Rate (RRR) of Mg relative to Si as a function of time for tremolite under variable pH conditions.

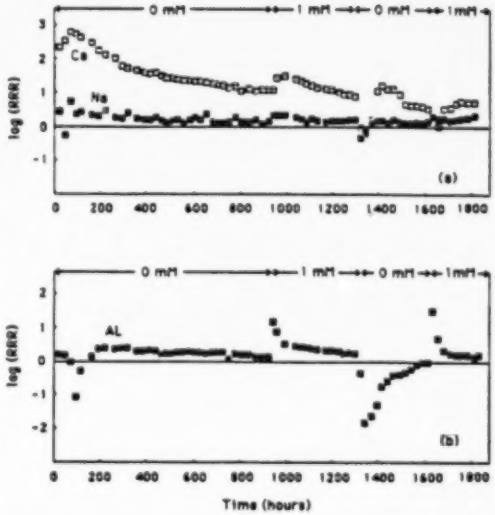

FIG. 12. Relative Reaction Rate (RRR) of (a) Ca and Na, (b) Al relative to Si as a function of time at pH 4 calculated for an An_{13} feldspar.

ratio to silicon for nearly 2000 hours before approaching congruency. During the dissolution of albite, CHOU and WOLLAST (1984) observed a large initial release of sodium due to a rapid exchange reaction, followed by a longer period of nonstoichiometric dissolution during which they proposed a leached layer was formed. Eventually, after steady state was established, the reaction tended to be congruent. HOLDREN and SPEYER (1985a) observed a similar pattern for the dissolution of an alkali feldspar. Initially both aluminum and base cations were released preferentially to silicon but eventually the reaction was stoichiometric in the pH range 5.5 to 9. Under more acidic conditions aluminum and cations were released in excess of silicon for several thousand hours, and congruency was never achieved. The authors gave no real explanation for this behavior; it is difficult to assess their results because they did not measure the composition of the feldspar, and cation concentrations were determined indirectly by measuring hydrogen ion consumption. Under acidic conditions, we also observed incongruent dissolution for long periods of time but found that the release of calcium eventually became congruent. In contrast to these results from dissolution of alkali feldspars, in our experiments on oligoclase calcium was the only component released in excess relative to silicon during the incongruent period of reaction. The excess release of calcium could be at least partially accounted for by the preferential dissolution of a calcium rich exsolved phase. Selective dissolution of calcium-rich regions of plagioclase during natural weathering has been documented by GARDNER (1983) and CLAYTON (1986). Recalculation of reaction stoichiometries using an An_{25} composition still indicates an excess release of calcium for several hundred hours. It is possible that calcium

is present in higher concentrations at dislocations or other sites preferentially attacked during dissolution. The core of the dislocation is ideal for the segregation of impurity atoms which are able to satisfy the charge imbalance and the dilation field introduced by the dislocation (HOBBS *et al.*, 1976). Because calcium has a higher charge and larger radius than sodium it may be better accommodated along these regions in the solid, and should be preferentially leached as the cores of dislocations are progressively "drilled out" during dissolution.

IMPLICATIONS

The rates of dissolution of oligoclase feldspar and tremolite are essentially independent of oxalate concentration at levels up to 1 mM. Oxalate is a very strong chelator for aluminum and other cations, and it is reasonable to extrapolate from these results to the suggestion that dissolved organic compounds in the concentrations commonly observed in soil solutions and surface waters will have a minimal effect on the dissolution rates of feldspars and amphiboles in dilute solution. The conclusion may not apply to more concentrated solutions which are not far from saturation with respect to the primary minerals. Further, since the rates of dissolution of oligoclase and tremolite are essentially independent of pH in the pH range typical of soil solutions, even the effect of organic acids on soil solution pH should have essentially no effect on the dissolution rate of these minerals. The effect of a change in the input of acid deposition from the atmosphere on the weathering rates of granitic rocks should thus be minor, although iron-containing hornblendes may respond somewhat differently from the tremolite used in our experiments.

These results also have implications for the broader question of the effects of vegetation, particularly the advent of higher land plants in the Ordovician or Silurian, on weathering rates. Plants can affect weathering rates in several ways. The most familiar effect is that they supply CO_2 and organic acids to the soil zone, which results in lower pH values and chelating anions in solution. Our results suggest that although this will have a large effect on translocation of aluminum and iron in the soil, the effect of pH and organic chelates on the dissolution rate of primary minerals will be minor, except perhaps in the immediate vicinity of fungi, where chemical conditions may be beyond the range of our experiments. Carbon dioxide and organic acids do, however, provide anions necessary for transport of cations released by weathering, and this should result in a significant acceleration of weathering rates. Plants also have an enormous influence on soil hydrology. They bind loose material on the land surface, creating a porous zone in which there will be prolonged contact between primary minerals and incoming precipitation (STALLARD, 1985). We would suggest that the effect of plants on soil hydrology has a much greater influence on weathering rates than their direct effects on soil solution chemistry.

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